

The Growth and Characterization of CuS Nanomaterials by Successive Ionic Layer Adsorption and Reaction (SILAR).

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ABSTRACT

The CuS thin films were grown by Successive Ionic Layer Adsorption and Reaction (SILAR) on glass substrates at room temperature. The effect of thickness on the treatment process was investigated. The optical properties such as absorbance, transmittance, extinction coefficient, refractive index, optical conductivity, absorption coefficient, and dielectric constants were studied. The electrical and structural properties of the films were also studied. The direct energy band gap of 2.16eV, 2.18eV, 2.21eV and 2.26eV were obtained for CuS films grown at 80, 100, 120 and 140 SILAR cycles. The XRD analysis indicates hexagonal structure (100) peak. Optical transmission measurements revealed that the films show good transparency in the visible region. The conductivity of the CuS films increases as the thickness increases.

(Keywords: thin films, CuS, deposition, optical and electrical properties, SILAR)

INTRODUCTION

The CuS thin films have been grown by Successive Ionic Layer Adsorption and Reaction (SILAR) technique. The solution growth techniques are simple, cheap and convenient for large area deposition and have easy controllable parameter. CuS are the significant binary compounds. They are well known to form a wide variety of non-stoichiometric and mixed phases, of which at least five species are known to be stable at room temperature: covellite (CuS) in the sulfur-rich region, and anilite ($\text{Cu}_{1.75}\text{S}$), digenite ($\text{Cu}_{1.8}\text{S}$), djurleite ($\text{Cu}_{1.95}\text{S}$) and Chalcocite (Cu_2S) in the copper-rich region [Koch et al, 1976].

As an important semiconductor with unique electronic, optical and chemical properties, they are of great concern due to its wide range of

applications in optical and electrical devices, such as photo-thermal conversion of solar energy, electro-conductive electrodes, microwave shielding coatings, solar control coatings, dye-sensitized solar cells, potential nanometer-scale switch, selective radiation filter on architectural windows, solar cells, cathode materials in lithium rechargeable batteries and some chemical sensing applications [Grozdanov et al., 1995, Huang et al., 1994, Lee et al., 2007, Sagade et al., 2008, Chung et al., 2002, Sakamoto et al., 2003, Sukarova et al., 1997 and Nair et al., 1991].

It has been reported that CuS can be transform into a superconductor below 1.6k due to its metallic conduction property [Tezuka et al., 2007]. Chemical methods have been used to grow CuS films. The shape, phase and the size of inorganic nano-crystals and micro-crystals are the determinant elements in varying their electrical, optical and other properties.

Physical deposition techniques are more suitable for synthesizing uniform and high quality films but they are correspondingly expensive and high energy consuming. They have the tendency of destroying the morphology of the films at high temperature above 500°C [Nair et al, 1991].

The chemical methods are economical and desirable structure can be obtained with them. Therefore, in order to grow CuS thin films with desirable shape and structure chemical method was employed. Several chemical techniques have been developed: the liquid-liquid interface reaction [Rao et al., 2007], chemical vapor deposition [Kemmler et al., 2002], electrochemical methods [Kuzuya et al., 2007], successive ionic layer adsorption and reaction [Pathan et al., 2002], atomic layer deposition [Johansson et al, 2002] and chemical bath deposition [Yuan et al, 2008].

The SILAR method is an aqueous solution method based on sequential reactions at substrate-solution interface for the deposition of the thin films. It involves the alternate dipping of the substrate into aqueous solution containing ions of each component. In the SILAR technique, quality films are obtained by optimizing some parameters such as concentration, temperature and pH of the precursor solutions and the time duration for adsorption, reaction and rinsing [Ates et al, 2009].

The structural and optical studies of CuS thin films showed a direct gap of 2.36eV and 2.2eV and hexagonal crystal structure. The electrical resistances of CuS films under illumination with tungsten lamp of 100Wm² have been reported and the resistance decreased with illumination [Nascus et al., 1997]. Due to unique property of hollow CuS structures, these structures are envisage to be used in novel building blocks for the advanced materials, solar cell devices and drug delivery system [Liu et al, 2009]. The XRD study showed that the as-grown CuS film reveals amorphous nature of the material. This film was annealed at 250°C in Ar ambient for two hours and characteristic peaks of CuS film begin to increase with annealing temperature. After annealing of this film, it reveals polycrystalline nature [Bagul et al, 2007].

MATERIALS AND METHODS

In this study, CuS thin films were grown on glass substrates by SILAR technique at room temperature. The adsorption, reaction and rinsing time were chosen experimentally to obtain a layer wise deposition and homogeneous thin films structure. One SILAR cycle involves four steps.

The experiment was carried out at different SILAR cycles 80, 100, 120 and 140 cycles so that varied thickness were obtained. The substrates were first cleaned using distilled water and later dried in air. The substrates were immersed in the first reaction beaker containing 0.1M copper chloride (pH 5.0). After 40 seconds, the substrates were moved to the rinsing beaker where they were washed with purified water for 30s. The substrates were removed from rinsing beaker and moved to reaction beaker containing 0.05 M sodium sulphide solution (Na₂S) with pH 12 where sulphide ions were adsorbed to the substrates for 40 seconds.

After anion adsorption, the substrates were moved to another beaker containing water where they were rinsed for second time for 30s. Hence, the first SILAR cycle is completed. Repeating these cycles 80 times, film with desired thickness were obtained. The substrates were cleaned for 10 min in acetone, dried and stored in desiccators. The experiment was repeated for the other cycles 100, 120 and 140 cycles. The thickness was measured using gravimetric method. The optical absorption spectra were measured using Janway 6405 UV/VIS spectrophotometer and the structural measurements were done using X-ray diffraction techniques.

RESULTS AND DISCUSSION

The deposition of CuS nano-materials was carried out at room temperature. The adhesion of copper thin films to the glass substrate was poor. During the deposition the color of the films was dark green. This color was the same with the color of bath solution. It was found that as the thickness increases the color became deeper. This could be attributed to the decrease of the optical transmittance in visible light range.

The optical transmittance of CuS thin films with different thickness in the wavelength range 300-900 nm was investigated. The optical transmittance spectral of CuS thin films is given in Figure 1. The CuS resulted from the least thickness exhibits the relatively highest transparency of about 41% at around 600nm in the visible light range and transparency decreases sharply with increasing the SILAR cycles. The increase in the thickness is considered to be the main factor of the reduction in transmittance.

The photo-absorption spectral of various CuS thin films is shown in Figure 2. The CuS thin film with lowest number of SILAR cycle exhibits the least photo-absorption ability. It was shown that CuS presented the good photo-absorption ability in the UV and IR regions. The films are characterized with high UV and IR absorption ability. The nano-materials are therefore exhibit low UV and IR transmittance. Thus, it could act as effective UV and IR filter. All optical absorption of the CuS films was nearly the same. The nonmaterial with highest SILAR cycles exhibit best photo-absorption ability.

The optical absorption spectral of the CuS thin films was shown in Figure 2. The absorbance spectra of the films were measured as a function of incident photon wavelength.

A blank substrate was placed on the reference beam for all measurement to correct the absorption of the substrate. The energy band gap of the thin film samples were calculated with the help of the $(\alpha h\nu)^2$ versus energy band gap values using the equation below.

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2} \quad (1)$$

where A is a constant and E_g is the the optical band gap. Thus, a plot of $(\alpha h\nu)^2$ versus $h\nu$ is a curve line whose intercept on the energy axis gives the energy gap. The band gap energy of the film have been determined by the extrapolation of the linear regions on the energy axis, $h\nu$. where E_g is the optical band gap, A is a constant. The band gap energy of the CuS thin film with 80, 100, 120 and 140 SILAR cycles are 2.26eV, 2.21eV, 2.18eV and 2.16eV respectively. The results of energy band gap of CuS thin films varied from 2.15eV and 2.26eV.

These results compare favourably with 2.16eV to 2.36eV obtained by Mudi et al, 2009 and 1.87eV to 2.03eV obtained by Ates et al, 2009. The band gap decreases as the thickness increases.

The absorption coefficient (α) associated with the strong absorption region of the film was calculated from absorbance (A) and the film thickness (t) using the relation:

$$\alpha = 2.303A/t \quad (2)$$

The extinction coefficient (k) is evaluated from the relation;

$$K = \alpha \lambda / 4\pi t \quad (3)$$

The optical conductivity of the thin films were evaluated by:

$$\sigma_o = \frac{\alpha n c}{4\pi} \quad (4)$$

where c is the velocity of light. Hence σ_o is the conductivity at the optical frequency concerned. In metals, σ_o and k are very high as reflectance approaches unity. In semiconductors k is usually small, σ_o is reduced and reflectance is also reduced thereby giving higher transparency than in metals. In the case of insulators, k is very small.

The dielectric constant is given by $\epsilon = \epsilon_r + \epsilon_i$:

$$\epsilon = (n + ik)^2 \quad (5)$$

where ϵ_r and ϵ_i are the real and imaginary parts respectively of ϵ and $(n+ik)$ is the complex refractive index. Hence,

$$\epsilon_r = n^2 - k^2 \quad (6)$$

$$\epsilon_i = 2ink \quad (7)$$

Where n is the refractive index and k is extinction coefficient [Wooten, 1972, Mahrov, et al, 2004].

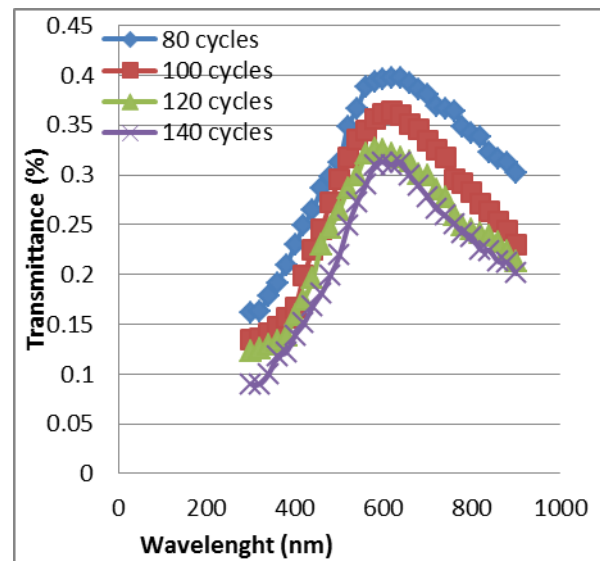


Figure 1: Transmittance Spectral of CuS Nanometers.

The graph of optical conductivity of the film samples against photon energy was plotted as shown in Figure 4. The optical conductivity of the thin films varies with photon energy in similar manner, increasing sharply from various values. The optical conductivity increases as the photon energy increases. The CuS films with 140 SILAR cycles exhibit the best optical conductivity. It has maximum optical conductivity of 0.8 at 2.16eV, 0.9 at 2.18eV, 1.1 at 2.21eV and 1.12 at 2.26eV.

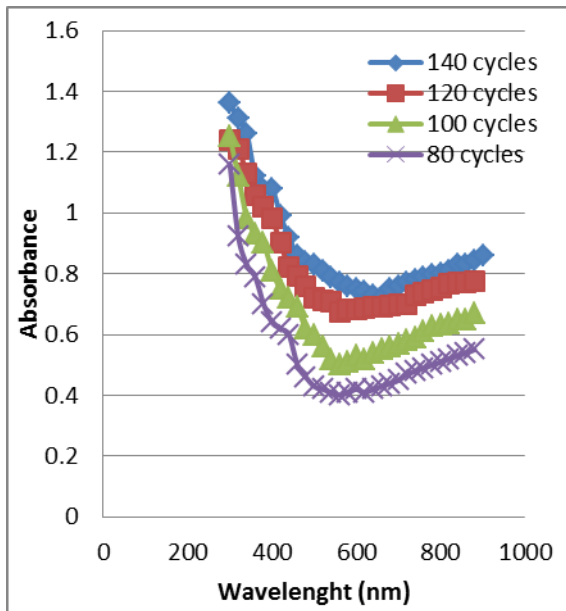


Figure 2: Absorbance Spectral of CuS Nanometers.

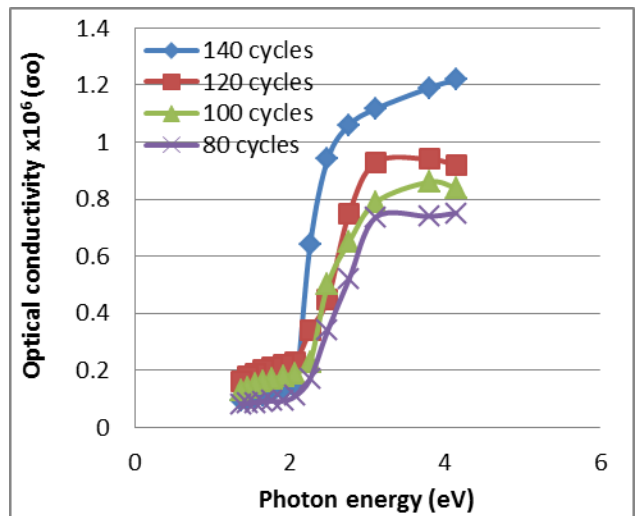


Figure 4: The optical conductivity Spectrals of CuS Nanometers.

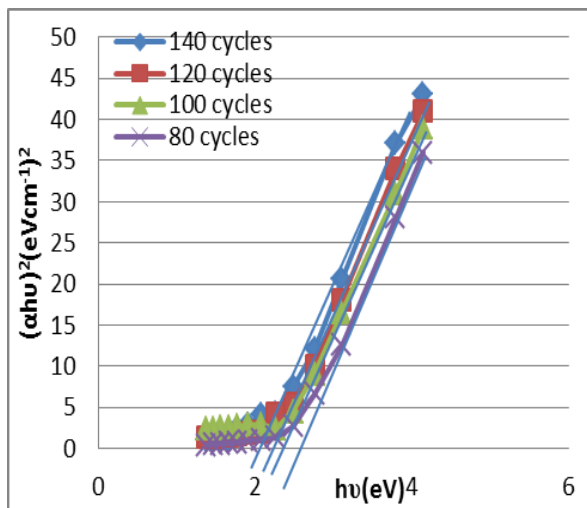


Figure 3: A Graph of $(\alpha h\nu)^2$ versus $h\nu$ for CuS Thin Films,

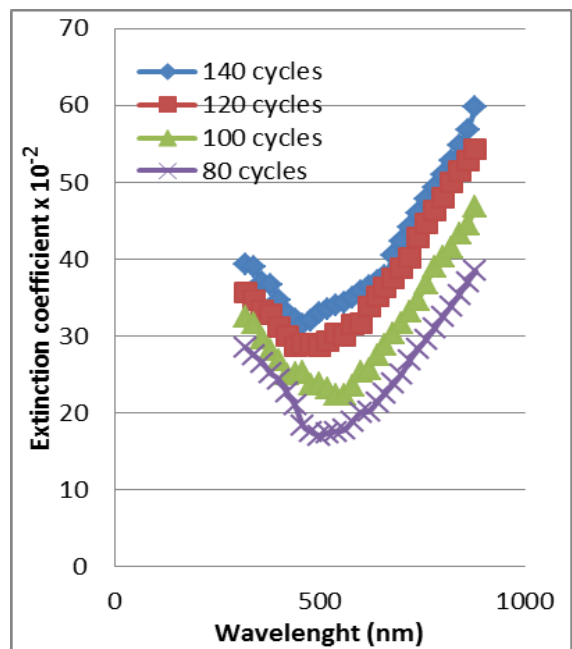


Figure 5: A Graph of Extinction Coefficient versus Wavelength of CuS Thin Films.

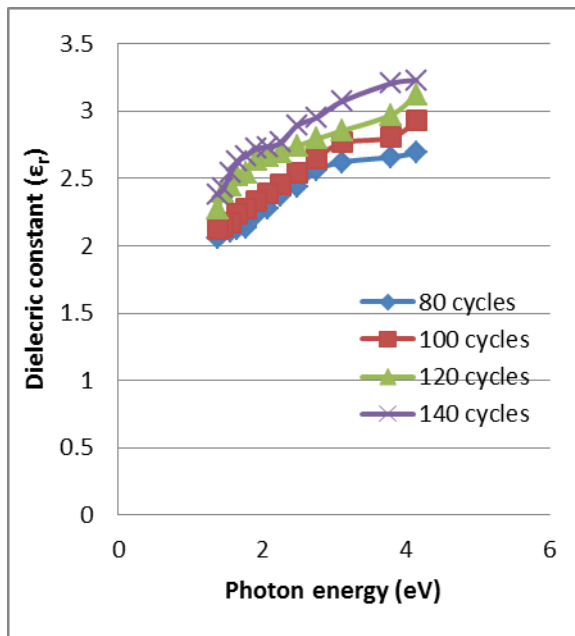


Figure 6: Plot of Dielectric Constant (real part) of CuS Nanomaterials.

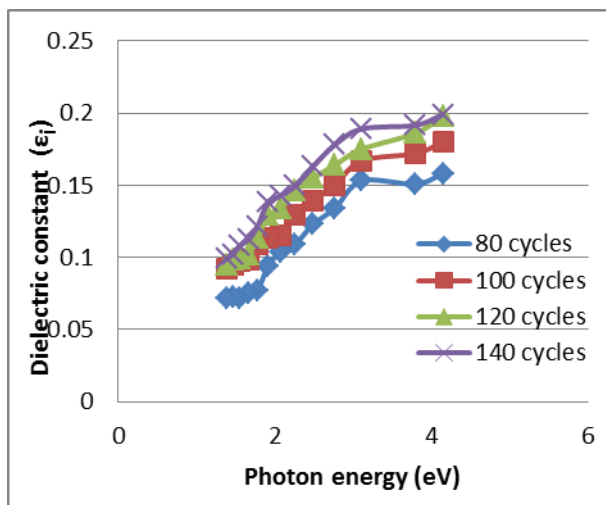


Figure 7: Plot of Dielectric Constant (imaginary part) of CuS Nanomaterials.

The graphs of the computed values of dielectric constant against photon energy are presented in Figure 6 and Figure 7. The imaginary dielectric constant of the specimens varies in similar manner, increasing from various values. The film grown at 140 cycles shows imaginary dielectric constant of 0.140 at 2.16eV, 0.145 at 2.18eV, 0.148 at 2.21eV and 0.15 at 2.26eV while the film grown with 80 cycles exhibit the least imaginary

dielectric constant. The dielectric constant decreases with decrease in thickness and increases with increase in photon energy. The CuS film grown with 140 cycles shows real dielectric constant of 2.75 at 2.16eV, 2.76 at 2.18eV, 2.77 at 2.21eV and 2.78 at 2.26eV.

The extinction coefficient of the CuS nanomaterials decreased from UV region to a minimum value of about 0.017 in the visible region and rises continuously in the IR region to a value of 0.06 in the NIR region as shown in the Figure 5.

The properties of high absorbance in the UV region and high transmittance in the VIS-NIR make the films good materials for the construction of poultry roofs and walls and coating for eye glasses for the protection of young chicks and the skin around the eyes respectively from the sun's burning due to UV radiation while the absorbance of infrared radiation helps to warm the inside of the poultry house which is needed for young chicks. The properties of high absorbance in the UV and NIR make the films good materials for thermal control window coatings and antireflection coatings. It could be used in architectural window to absorb UV and IR and allow only visible light into the house.

Since n and k decreases with increasing wavelength in the visible region, this behavior indicates that the transparent films seem to behave like transparent insulators. Transparent insulators are expected to prevent high energy UV and high temperature NIR radiation into a building while allowing only visible light.

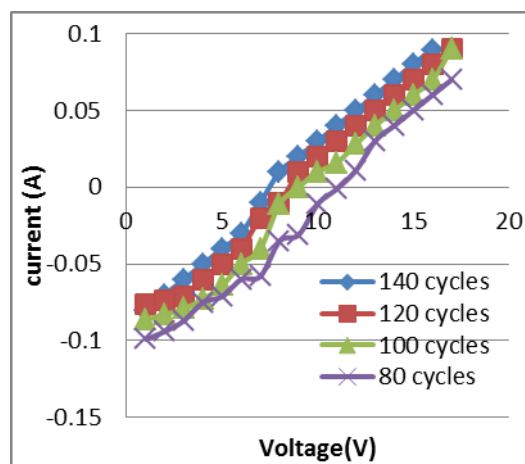


Figure 8: I/V Characteristics of CuS Thin Films.

The I/V characteristics of CuS nanometers is shown in Figure 8. The characteristics are linear indicating the ohmic contact of electrodes with aggregate films. After the investigations and calculations, the resistivity and conductivity values of CuS thin films were determined as shown in Table 2. Increasing the thickness of the films result in the decrease of the relative amount of insulating gaps between the aggregated particle areas. The conductivity therefore increases while the resistivity decreases.

Table 1: The Optical Band Gap of CuS Thin Films.

SILAR cycles	CuS band gap(eV)
80	2.26
100	2.21
120	2.18
140	2.16

Table 2: Electrical Parameters of CuS Thin Films.

Thickness (nm)	Resistivity (Ωcm)	Conductivity (Ωcm) ⁻¹
7.25	17.05	0.058
12.35	14.55	0.068
19.43	14.14	0.071
26.06	3.482	0.29

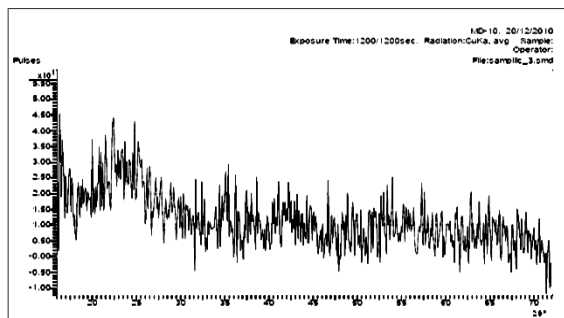


Figure 8: XRD Spectra of CuS with 80 Cycles.

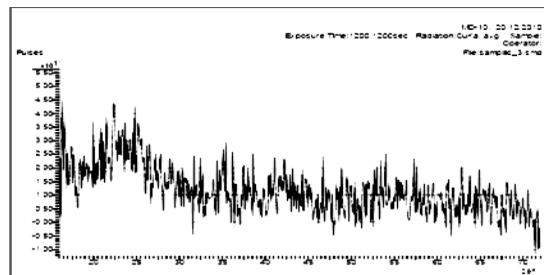


Figure 9: XRD Spectra of CuS Film with 100 Cycles.

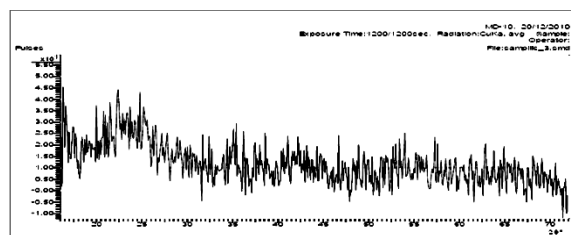


Figure 10: XRD Spectra of CuS Film with 120 Cycles.

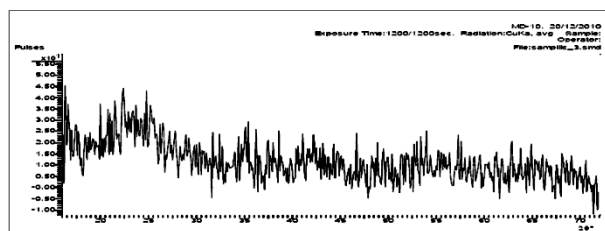


Figure 11: XRD Spectra of CuS Film with 140 Cycles.

The structural analysis of CuS thin films was carried out by using X-ray diffractometer. The X-ray diffraction patterns of the CuS thin films, grown at different SILAR cycles on glass substrates are shown in Figures 8 - 11.

The XRD analysis shows that the thin films are single phase CuS with lattice parameters $a = 3.7928\text{\AA}$ and $c = 16.346\text{\AA}$ which is almost in agreement with the standard data from JCPDS card No 78-2121. There is no difference among the XRD patterns of the nano-materials. The planes are oriented in the direction (110), (103), (102), (108) and (100).

The films exhibit hexagonal crystal structure. The highest intensity peak corresponds to (100) preferred orientation. The (100) peak is stronger than other peaks. In general, the preferential orientation of the films is along the (100)

direction. However, the XRD spectrum of the CuS layer deposited by SILAR technique from aqueous only exhibit the (100) direction.

The energy-dispersive analysis by X-ray has been used also to determine the composition of CuS thin films. The analysis confirms the presence of Cu and S in the deposited film with Cu \approx 39.05 and S \approx 60.95. It confirms that the films are sulfur (S) rich.

CONCLUSION

The Successive Ionic Layer Adsorption and Reaction (SILAR) technique was used to deposit CuS thin films on glass substrates. The variations on the films structure, thickness, dielectric constant, electrical and optical properties were investigated. The optical band gap decreases as the thickness increased and the current values increased as the thickness increases.

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